

VERIFICATION OF TRANSLATION

I, Yasuo Yasutomi of Chuo BLDG., 4-20, Nishinakajima 5-chome,  
Yodogawa-ku, Osaka-shi, Osaka 532-0011 JAPAN, hereby declare that I am  
conversant with the Japanese and English languages and that I am the  
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translation of the Japanese Patent Application No. Hei 10-151571  
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Yasuo Yasutomi

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[Title of the Invention] POLYMER AND METHOD OF PRODUCING POLYMER

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[Inventor]

[Address or Residence] c/o Kobe Research Laboratories Research  
Institute of Kaneka Corporation  
2-80, Yoshidacho 1-chome, Hyogo-ku,  
Kobe-shi, HYOGO

[Name] NAKAGAWA Yoshiki

[Inventor]

[Address or Residence] c/o Kobe Research Laboratories Research  
Institute of Kaneka Corporation  
2-80, Yoshidacho 1-chome, Hyogo-ku,  
Kobe-shi, HYOGO

[Name] KITANO Kenichi

[Inventor]

[Address or Residence] c/o Kobe Research Laboratories Research  
Institute of Kaneka Corporation  
2-80, Yoshidacho 1-chome, Hyogo-ku,  
Kobe-shi, HYOGO

[Name] FUJITA Masayuki

[Applicant]

[Identification Number] 000000941

[Name] KANEKA CORPORATION

[Representative] FURUTA Takeshi

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[List of Attached Documents]

[Document Name]	Description	1
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[Document Name]	Abstract	1
[Necessity of Proof]	Needed	

[Document Name] Description

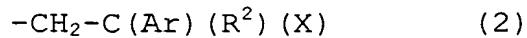
[Title of the Invention] POLYMER AND METHOD OF PRODUCING  
POLYMER

[Scope of Claims for Patent]

5 [Claim 1] A multiblock copolymer which is produced by adding a polymer (I) containing a group represented by the general formula 1:



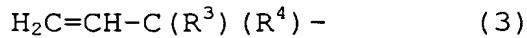
(wherein  $\text{R}^1$  represents a hydrogen atom or a hydrocarbon group 10 containing 1 to 20 carbon atoms) at one terminus, and a group represented by the general formula 2:



15 (wherein Ar represents an aryl group which may optionally contain a substituent,  $\text{R}^2$  represents a hydrogen atom or a methyl group, and X represents chlorine, bromine or iodine) at the other terminus

to a living radical polymerization system.

20 [Claim 2] The multiblock copolymer according to Claim 1, wherein the group represented by the general formula 1 is a group represented by the general formula 3:



(wherein  $\text{R}^3$  and  $\text{R}^4$  may be the same or different and each represents a hydrogen atom or a monovalent organic group).

25 [Claim 3] The multiblock copolymer according to Claim 1, wherein, in the general formula 1,  $\text{R}^1$  is a hydrogen atom.

[Claim 4] The multiblock copolymer according to Claims 1 to 3, wherein, in the general formula 2,  $\text{R}^2$  is a hydrogen atom.

[Claim 5] The multiblock copolymer according to Claims 1 to 4, wherein the polymer (I) is a styrenic polymer.

30 [Claim 6] The multiblock copolymer according to any of Claims 1 to 4, wherein the polymer (I) is a (meth)acrylic polymer.

[Claim 7] The multiblock copolymer according to Claims 1 to 6, wherein the polymer (I) has a glass transition point of not lower than 25°C.

35 [Claim 8] The multiblock copolymer according to any of Claims

1 to 7, wherein the polymer (I) has the number average molecular weight of 500 to 100000.

[Claim 9] The multiblock copolymer according to Claims 1 to 8, wherein the polymer (I) has the ratio between the weight average molecular weight ( $M_w$ ) and the number average molecular weight ( $M_n$ ) ( $M_w/M_n$ ) as determined by gel permeation chromatography of not more than 1.8.

[Claim 10] The multiblock copolymer according to any of Claims 1 to 9, wherein the polymer (I) is produced by controlled radical polymerization.

[Claim 11] The multiblock copolymer according to Claim 10, wherein the polymer (I) comprises a vinyl polymer produced by polymerizing a vinyl monomer using an organic halide or a sulfonyl halide as an initiator, and a metal complex containing an element of the group 8, 9, 10 or 11 of the periodic table as a central metal as a catalyst.

[Claim 12] The multiblock copolymer according to Claim 11, wherein the metal complex to serve as a catalyst for producing the polymer (I) is a copper, nickel, ruthenium or iron complex.

[Claim 13] The multiblock copolymer according to Claim 12, wherein the metal complex to serve as a catalyst for producing the polymer (I) is a copper complex.

[Claim 14] The multiblock copolymer according to Claim 10, wherein the polymer (I) comprises a vinyl polymer produced by polymerizing a vinyl monomer using a chain transfer agent.

[Claim 15] The polymer according to Claims 11 to 13, wherein the polymer (I) is produced by using an alkenyl-containing organic halide or a sulfonyl halide as an initiator.

[Claim 16] The multiblock copolymer according to Claim 15, wherein the polymer (I) is produced by using an allyl halide as an initiator.

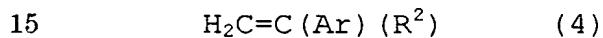
[Claim 17] The multiblock copolymer according to Claims 11 to 13, wherein the polymer (I) is produced by converting an initiator-derived functional group present at a terminus of a polymer obtained by starting polymerization by a functional

group-containing initiator to the group represented by the general formula 1.

[Claim 18] The multiblock copolymer according to Claim 17, wherein the functional group in the functional group-containing 5 initiator contains a hydroxyl group.

[Claim 19] The multiblock copolymer according to Claim 18, which is obtainable by converting a hydroxyl group by a compound having both the group represented by the general formula 1 and an isocyanate group.

10 [Claim 20] The multiblock copolymer according to Claims 11 to 13 and 15 to 19, wherein the polymer (I) is produced by introducing the group represented by the general formula 2 to a polymer terminus by adding and polymerizing a monomer represented by the general formula 4:



(wherein Ar represents an aryl group which may optionally have a substituent, and R<sup>2</sup> represents a hydrogen atom or a methyl group) at the time of completion of living radical polymerization.

20 [Claim 21] The multiblock copolymer according to Claims 1 to 20, wherein a polymer chain produced by the living cationic polymerization has a glass transition point not higher than 25°C.

[Claim 22] The multiblock copolymer according to Claim 21, 25 wherein the polymer (I) is added to a living cationic polymerization system of isobutylene.

[Claim 23] The multiblock copolymer according to Claims 1 to 22, wherein the living cationic polymerization is started from a di- or more functional initiator.

30 [Claim 24] The multiblock copolymer according to Claims 1 to 23, wherein the living cationic polymerization is carried out in a solvent without containing methylene chloride.

[Claim 25] The multiblock copolymer according to Claim 24, 35 wherein the living cationic polymerization is carried out in a solvent containing toluene.

[Claim 26] The multiblock copolymer according to Claims 1 to 25, wherein the polymer (I) is used as an initiator of the living cationic polymerization.

5 [Claim 27] The multiblock copolymer according to Claims 1 to 25, wherein the polymer (I) is added in course of the living cationic polymerization.

10 [Claim 28] The multiblock copolymer according to Claims 1 to 25, wherein the polymer (I) is added after completion of the living cationic polymerization, and a cationically polymerizable monomer is added at that point or after the addition.

15 [Claim 29] A thermoplastic elastomer which comprises, as the main component thereof, the polymer according to Claims 1 to 28.

15 [Claim 30] An impact resistance improving agent which comprises, as the main component thereof, the polymer according to Claims 1 to 28.

[Detailed Description of the Invention]  
[0001]

20 [Technical Field of the Invention]

The present invention relates to a method for producing a multiblock copolymer which comprises adding a polymer containing an alkenyl group to which a growing terminus of living cationic polymerization can be added at one terminus and 25 containing a group serving as an initiator for living cationic polymerization at other terminus to a living radical polymerization system, the polymer, and its use.

[0002]

[Prior Art]

30 Block copolymers composed of different polymer block species bound to each other are generally produced by polymerizing different monomer species in succession. Heretofore, various methods of polymerization have been developed and attempts have been made to produce block 35 copolymers using them. When cationic polymerization is

employed, however, it is difficult to control the polymerization, since the growing species carbenium ion is unstable. In recent years, examples of the so-called living cation polymerization in which the growing carbenium ion in the 5 cationic polymerization is inhibited from undergoing isomerization, chain transfer reaction or termination reaction have been reported. For example, Higashimura et al. (Macromolecules, 17, 265, 1984) report that cationic living polymerization is possible in vinyl ether polymerization using 10 a combination of hydrogen iodide and iodine as an initiator. However, the polymerization using such initiator has various problems; for instance, its application is restricted to those monomers which have an alkoxy group high in electron donating ability and are highly susceptible to cationic polymerization, 15 and the initiator is unstable and difficult to handle.

[0003]

On the other hand, Kennedy et al. (Japanese Kokai Publication Sho-62-48704, Japanese Kokai Publication Sho-64-62308), by polymerizing olefin monomers, such as 20 isobutylene, using an organic carboxylic acid or an ester, or an ether as an initiator in combination with a Lewis acid, showed that cationic living polymerization is possible with olefin monomers as well. This method has been modified in several ways, and Nippon Zeon (Japanese Kokoku Publication Hei-07-59601) has 25 succeeded in obtaining block copolymers by successive monomer addition with additional use of an amine. In this modification, isobutylene-based block copolymers comprising an isobutylene polymer and a styrene polymer are produced in a mixed solvent composed of methylene chloride and hexane. However, such 30 halogenated hydrocarbons containing 1 or 2 carbon atoms have problems; for instance, they are difficult to handle, and require large scale equipment for preventing them from being discharged into the environment to raise the cost of production. Although, on the other hand, such polymerization is also 35 possible in a halogen-free solvent such as toluene, very fine

adjustment is required, depending on the monomer, for the monomer to show adequate polarity. It is thus very difficult to establish the conditions for successive polymerization of two or more monomer species differing in reactivity.

5 [0004]

Among block copolymers, while multiblock copolymers in which many polymer blocks are bonded have characteristics of block copolymers such as thermoplastic elastomers, as well as have higher molecular weight than block copolymers of ABA type 10 or the like, and are expected to have high strength and stability. However, it is not easy to produce such a multiblock copolymer in conventional methods.

[0005]

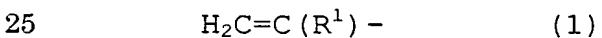
[Subject which the Invention is to Solve]

15 The present invention has for its object to provide a method for easily producing a multiblock copolymer composed of any of various polymers and a cationic polymerization polymer without requiring optimization of polymerization conditions which is difficult to achieve.

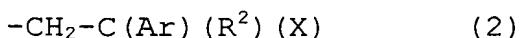
20 [0005]

[Means for Solving the Problems]

The present invention relates to a multiblock copolymer which is produced by adding a polymer (I) containing a group represented by the general formula 1:



(wherein  $R^1$  represents a hydrogen atom or a hydrocarbon group containing 1 to 20 carbon atoms) at one terminus, and a group represented by the general formula 2:

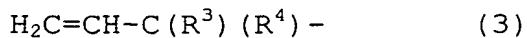


30 (wherein Ar represents an aryl group which may optionally have a substituent,  $R^2$  represents a hydrogen atom or a methyl group, and X represents chlorine, bromine or iodine) at other terminus

to a living radical polymerization system.

35 [0007]

To the group represented by the general formula 1 in the polymer (I), a growing terminus of living cationic polymerization is added, and the group represented by the general formula 2 serves an initiator for living cationic polymerization. As the result, a multiblock copolymer is produced. Therefore, preferably, the group represented by the general formula 1 has a terminus to which a growing terminus for living cationic polymerization is added but is hardly undergo polymerization, and the group represented by the general formula 3 is preferred:



(wherein  $\text{R}^3$  and  $\text{R}^4$  may be the same or different and each represents a hydrogen atom or a monovalent organic group).  
[0008]

The polymer (I) is preferably polymerized by controlled radical polymerization, and more preferably by living radical polymerization. The terminal group is introduced by the initiator, functional group conversions or the like. The polymer (I) also has a characteristic for having a narrow molecular weight distribution.

The living cationic polymerization system to which the polymer (I) is added is not particularly restricted, but preferred is a system polymerizing isobutylene monomers.

[0009]

The multiblock copolymer of the present invention is useful as a thermoplastic elastomer or an impact resistance improving agent.

[0010]

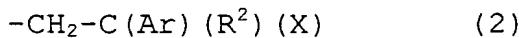
#### [Embodiment of the Invention]

The present invention relates to a multiblock copolymer which is produced by adding a polymer (I) containing a group represented by the general formula 1:



(wherein  $\text{R}^1$  represents a hydrogen atom or a hydrocarbon group containing 1 to 20 carbon atoms) at one terminus, and a group

represented by the general formula 2:

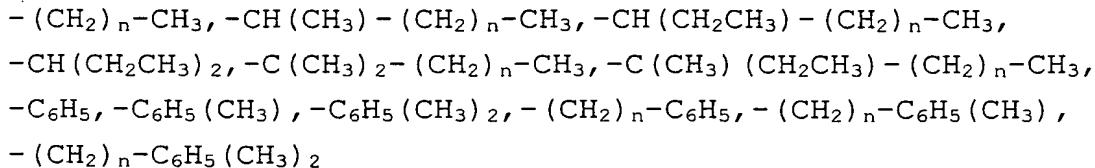


(wherein Ar represents an aryl group which may optionally have a substituent, R<sup>2</sup> represents a hydrogen atom or a methyl group, and X represents chlorine, bromine or iodine) at other terminus

5 to a living radical polymerization system.

[0011]

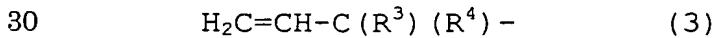
In the general formula 1, R<sup>1</sup> is a hydrogen atom or a hydrocarbon group containing 1 to 20 carbon atoms, specifically including, for example, the following groups:



(wherein n is an integer not smaller than 0 and the total number of carbon atoms in each group is not greater than 20). Among these, a hydrogen atom is preferred.

[0012]

To the group represented by the general formula 1 in the polymer (I), a growing terminus for living cationic polymerization is added, and the group represented by the general formula 2 serves an initiator for living cationic polymerization. As the result, a multiblock copolymer is produced. Therefore, preferably, the group represented by the general formula 1 has a terminus to which a growing terminus for living cationic polymerization is added but is hardly undergo polymerization, and the group represented by the general formula 3 is preferred:



(wherein R<sup>3</sup> and R<sup>4</sup> may be the same or different and each represents a hydrogen atom or a monovalent organic group).

[0013]

In the general formula 2, R<sup>2</sup> is a hydrogen atom or a methyl group, and preferably is a hydrogen atom. Ar is an aryl group

which may optionally have a substituent, and is not particularly restricted, but there may be mentioned the following groups:

$C_6H_5-$ ,  $\text{o}, \text{m}, \text{p}-\text{(CH}_3\text{)}C_6H_4-$ ,  $2,6-\text{(CH}_3\text{)}_2C_6H_3-$ ,  $2,4-\text{(CH}_3\text{)}_2C_6H_3-$ ,

$2,4,6-\text{(CH}_3\text{)}_3C_6H_2-$ ,  $\text{o}, \text{m}, \text{p}-ClC_6H_4-$ ,  $2,6-Cl_2C_6H_3-$ ,  $2,4-Cl_2C_6H_3-$ ,

5  $2,4,6-Cl_3C_6H_2-$ ,  $\text{o}, \text{m}, \text{p}-\text{(tert-C}_4H_9\text{)}C_6H_4-$ ,  $\text{o}, \text{m}, \text{p}-\text{(CH}_3O\text{)}C_6H_4-$ , Np-  
(Np is a naphthyl group).

X represents chlorine, bromine or iodine, and preferably chlorine or bromine.

<Monomer >

10 The main chain of the polymer (I) of the present invention is not restricted, but preferably a vinyl polymer. The vinyl monomer constituting the polymer is not particularly restricted and various ones may be used. Examples are (meth)acrylic monomers such as (meth)acrylic acid, methyl (meth)acrylate, 15 ethyl (meth)acrylate, n-propyl (meth)acrylate, isopropyl (meth)acrylate, n-butyl (meth)acrylate, isobutyl (meth)acrylate, tert-butyl (meth)acrylate, n-pentyl (meth)acrylate, n-hexyl (meth)acrylate, cyclohexyl (meth)acrylate, n-heptyl (meth)acrylate, n-octyl 20 (meth)acrylate, 2-ethylhexyl (meth)acrylate, nonyl (meth)acrylate, decyl (meth)acrylate, dodecyl (meth)acrylate, phenyl (meth)acrylate, toluyl (meth)acrylate, benzyl (meth)acrylate, 2-methoxyethyl (meth)acrylate, 3-methoxybutyl (meth)acrylate, 2-hydroxyethyl (meth)acrylate, 25 2-hydroxypropyl (meth)acrylate, stearyl (meth)acrylate, glycidyl (meth)acrylate, 2-aminoethyl (meth)acrylate,  $\gamma$ - (methacryloyloxypropyl)trimethoxysilane, (meth)acrylic acid-ethylene oxide adducts, trifluoromethylmethyl (meth)acrylate, 2-trifluoromethylmethylethyl (meth)acrylate, 30 2-perfluoroethylmethylethyl (meth)acrylate, 2-perfluoroethyl-2-perfluorobutylethyl (meth)acrylate, 2-perfluoroethyl (meth)acrylate, perfluoromethyl (meth)acrylate, diperfluoromethylmethyl (meth)acrylate, 2-perfluoromethyl-2-perfluoroethylmethyl (meth)acrylate, 35 2-perfluorohexylethyl (meth)acrylate, 2-perfluorodecylethyl

(meth)acrylate and 2-perfluorohexadecylethyl (meth)acrylate; styrenic monomers such as styrene, vinyltoluene,  $\alpha$ -methylstyrene, chlorostyrene, styrenesulfonic acid and salts thereof; fluorine-containing vinyl monomers such as  
5 perfluoroethylene, perfluoropropylene and vinylidene fluoride; silicon-containing vinyl monomers such as vinyltrimethoxysilane and vinyltriethoxysilane; maleic anhydride, maleic acid, maleic acid monoalkyl esters and dialkyl esters; fumaric acid, fumaric acid monoalkyl esters and  
10 dialkyl esters; maleimide monomers such as maleimide, methylmaleimide, ethylmaleimide, propylmaleimide, butylmaleimide, hexylmaleimide, octylmaleimide, dodecylmaleimide, stearylmaleimide, phenylmaleimide and cyclohexylmaleimide; nitrile group-containing vinyl monomers  
15 such as acrylonitrile and methacrylonitrile; amide group-containing vinyl monomers such as acrylamide and methacrylamide; vinyl esters such as vinyl acetate, vinyl propionate, vinyl pivalate, vinyl benzoate and vinyl cinnamate; alkenes such as ethylene and propylene; conjugated dienes such  
20 as butadiene and isoprene; vinyl chloride, vinylidene chloride, allyl chloride, allyl alcohol and so on. These may be used singly or a plurality thereof may be copolymerized. Among them, styrenic monomers and (meth)acrylic monomers are preferred from the viewpoint of physical properties of the products.  
25 [0014]

The molecular weight distribution, namely the ratio of weight average molecular weight to number average molecular weight as determined by gel permeation chromatography, in the polymer (I) of the present invention is not particularly restricted but is preferably not more than 1.8, more preferably not more than 1.6, and most preferably not more than 1.3.

The number average molecular weight of the polymer (I) of the present invention is not particularly restricted but is preferably within the range of 500 to 1,000,000, more preferably 35 within the range of 3,000 to 40,000.

The glass transition point of the polymer (I) is preferably not lower than 25°C in view of physical properties of the product multiblock copolymer and the like.

<Method of producing the polymer (I)>

5       The method of producing the polymer (I) is not particularly restricted but said polymer is preferably produced by controlled radical polymerization. As the controlled radical polymerization, there may be mentioned polymerization which comprises using a chain transfer agent, or living radical  
10      polymerization which has been recently developed. The latter is preferable from the polymerization controllability point of view.

[0015]

15      The method of introducing the groups represented by the general formula 1 and 2 to the terminus of the polymer (I) is not particularly restricted. As for the introduction method of the group represented by the general formula 1, there may be mentioned a method comprising carrying out living radical polymerization using an initiator containing the group of the general formula 1, and a method comprising introducing the group of the general formula 1 by functional group conversion after polymerization using an initiator containing a functional group other than the general formula 1, and the like. As for the group of the general formula 2, there may be mentioned a method comprising polymerization of a styrenic monomer, a method comprising polymerization by adding a styrenic monomer after polymerization of a monomer other than styrenic monomers.  
25

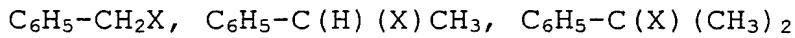
<Living radical polymerization>

30      Living radical polymerization is radical polymerization in which the activity of the polymerization terminus is maintained without being loosed. In its narrow sense, the term "living polymerization" means that polymerization in which a terminus always retain activity. Generally, however, it also includes, within the meaning thereof, pseudoliving polymerization in which terminally inactivated molecules and

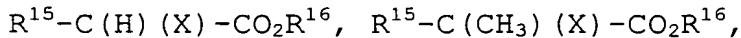
terminally activated ones are in equilibrium. The latter definition is to be applied to the present invention. Living radical polymerization has recently been aggressively investigated by a number of groups. As examples, there may be mentioned, among others, the method which uses a chain transfer agent such as polysulfide, the method which uses cobalt porphyrin complex (Journal of the American Chemical Society, 1994, vol. 116, page 7943), the method which uses a radical capping agent, for example a nitroxide compound (Macromolecules, 1994, vol. 27, page 7228), and atom transfer radical polymerization (ATRP) in which an organic halide, for instance, is used as an initiator and a transition metal complex as a catalyst. In the present invention, it is not particularly restricted as for which method is to be used, but atom transfer radical polymerization is preferred in view of easy controllability. In atom transfer radical polymerization, polymerization is carried out by using an organic halide or a sulfonyl halide as an initiator, and a metal complex containing an element of the group 8, 9, 10 or 11 of the periodic table as a central metal as a catalyst (for example, refer to Matyjaszewski et al., the Journal of the American Chemical Society, 1995, vol. 117, page 5614; Macromolecules, 1995, vol. 28, page 7901; Science, 1996, vol. 272, page 866; or Sawamoto et al., Macromolecules, 1995, vol. 28, page 1721). By these methods, polymerization proceeds as living polymerization and give polymers narrow in molecular weight distribution ( $M_w/M_n$  being about 1.1 to 1.5) and the molecular weight can arbitrarily be controlled by means of the charge ratio between the monomer and initiator, although they involve a radical polymerization generally having a very high rate of reaction and a tendency toward termination resulting from coupling of radicals with each other. Moreover, as the name "atom transfer radical polymerization" shows, generally, a halogen group derived from an initiator is present at a growing terminus of the polymer.

35 <Initiator>

The organic halide or a sulfonyl halide compound used in the atom transfer radical polymerization specifically include, among others:

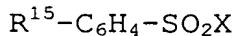


- 5 (in the above chemical formulas,  $\text{C}_6\text{H}_5$  is a phenyl group and X is chlorine, bromine or iodine);



(in which  $\text{R}^{15}$  represents a hydrogen atom or an alkyl group having

- 10 1 to 20 carbon atoms, an aryl group having 6 carbon atoms or an aralkyl group having 7 to 20 carbon atoms, X is chlorine, bromine or iodine, and  $\text{R}^{16}$  represents a monovalent organic group having 1 to 20 carbon atoms); and



- 15 (in which  $\text{R}^{15}$  is a hydrogen atom or an alkyl group having 1 to 20 carbon atoms, an aryl group having 6 to 20 carbon atoms or aralkyl group having 7 to 20 carbon atoms and X is chlorine, bromine or iodine).

[0016]

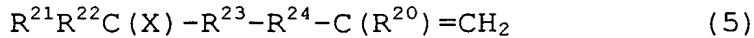
- 20 Furthermore, when an organic halide or sulfonyl halide having a functional group other than the functional group for initiating polymerization is used as the initiator, a polymer introduced with a functional group at its terminus can be easily obtained. As such functional group, there may be mentioned

- 25 alkenyl, hydroxyl, epoxy, amino, amide and silyl groups, among others. By introducing the group represented by the general formula 1 to the polymer produced from an initiator containing such functional group by various methods described later to produce the polymer (I), and adding the polymer to the living 30 radical polymerization system, a block copolymer containing carious functional group at its terminus can be easily obtained.

[0017]

- When an alkenyl-containing initiator is used, the polymer (I) containing the group represented by the general formula 1 can be easily obtained. The alkenyl-containing organic halide

is not restricted but may be one having the structure shown by the general formula 5:



(wherein  $R^{20}$  is a hydrogen atom or a methyl group,  $R^{21}$  and  $R^{22}$  each is a hydrogen atom or a monovalent alkyl having 1 to 20 carbon atoms, an aryl group having 6 to 20 carbon atoms or an aralkyl group and  $R^{21}$  and  $R^{22}$  may be bound to each other at respective other termini,  $R^{23}$  is  $-C(O)O-$  (ester group),  $-C(O)-$  (keto group) or an o-, m- or p-phenylene group,  $R^{24}$  is a direct bond or a divalent organic group having 1 to 20 carbon atoms, which may optionally contain one or more ether bonds, and X is chlorine, bromine or iodine).

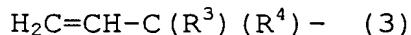
In these compounds, carbon to which a halogen is bound is bound to a carbonyl or phenyl group, thereby polymerization is started after the carbon-halogen bond is activated.

[0018]

As specific examples of the substituents  $R^{21}$  and  $R^{22}$ , there may be mentioned hydrogen, methyl, ethyl, n-propyl, isopropyl, n-butyl, pentyl, hexyl, etc.  $R^{21}$  and  $R^{22}$  may be bound to each other at respective other termini to form a cyclic skeleton. In such case,  $-R^{21}-R^{22}-$  may be, for example,  $-CH_2CH_2-$ ,  $-CH_2CH_2CH_2-$ ,  $-CH_2CH_2CH_2CH_2-$  and the like.

[0019]

The alkenyl group preferably has a terminus to which a growing terminus of the living cationic polymerization is added but hardly undergo polymerization as mentioned above, and preferred is a group represented by the general formula 3:



(wherein  $R^3$  and  $R^4$  may be the same or different and each represents a hydrogen atom or a monovalent organic group).

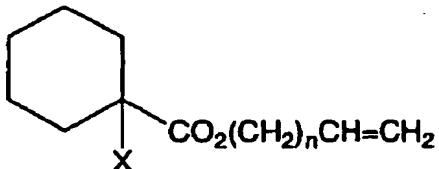
[0020]

As specific examples of the alkenyl-containing organic halide represented by the general formula 5, there may be mentioned the following:

$XCH_2C(O)O(CH_2)_nCH=CH_2$ ,

$\text{H}_3\text{CC}(\text{H})(\text{X})\text{C}(\text{O})\text{O}(\text{CH}_2)_n\text{CH}=\text{CH}_2$ ,  
 $(\text{H}_3\text{C})_2\text{C}(\text{X})\text{C}(\text{O})\text{O}(\text{CH}_2)_n\text{CH}=\text{CH}_2$ ,  
 $\text{CH}_3\text{CH}_2\text{C}(\text{H})(\text{X})\text{C}(\text{O})\text{O}(\text{CH}_2)_n\text{CH}=\text{CH}_2$   
[0021]

5 [Chemical 1]



10 [0022]

(in the above formulas, X is chlorine, bromine or iodine and n is an integer of 0 to 20, n is preferably an integer of 1 to 20);

$\text{XCH}_2\text{C}(\text{O})\text{O}(\text{CH}_2)_n\text{O}(\text{CH}_2)_m\text{CH}=\text{CH}_2$ ,

15  $\text{H}_3\text{CC}(\text{H})(\text{X})\text{C}(\text{O})\text{O}(\text{CH}_2)_n\text{O}(\text{CH}_2)_m\text{CH}=\text{CH}_2$ ,

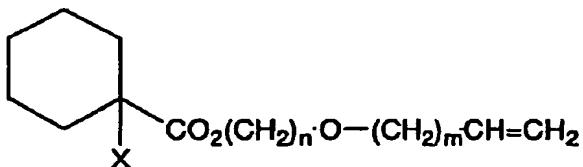
$(\text{H}_3\text{C})_2\text{C}(\text{X})\text{C}(\text{O})\text{O}(\text{CH}_2)_n\text{O}(\text{CH}_2)_m\text{CH}=\text{CH}_2$ ,

$\text{CH}_3\text{CH}_2\text{C}(\text{H})(\text{X})\text{C}(\text{O})\text{O}(\text{CH}_2)_n\text{O}(\text{CH}_2)_m\text{CH}=\text{CH}_2$ ,

[0023]

[Chemical 2]

20



[0024]

25 (in the above formulas, X is chlorine, bromine or iodine, n is an integer of 1 to 20, and m is an integer of 0 to 20; m is preferably an integer of 1 to 20);

$\text{o}, \text{m}, \text{p}-\text{XCH}_2-\text{C}_6\text{H}_4-(\text{CH}_2)_n-\text{CH}=\text{CH}_2$ ,

$\text{o}, \text{m}, \text{p}-\text{CH}_3\text{C}(\text{H})(\text{X})-\text{C}_6\text{H}_4-(\text{CH}_2)_n-\text{CH}=\text{CH}_2$ ,

30  $\text{o}, \text{m}, \text{p}-\text{CH}_3\text{CH}_2\text{C}(\text{H})(\text{X})-\text{C}_6\text{H}_4-(\text{CH}_2)_n-\text{CH}=\text{CH}_2$ ,

(in the above formulas, X is chlorine, bromine or iodine and n is an integer of 0 to 20; n is preferably an integer of 1 to 20);

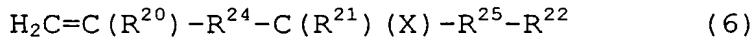
$\text{o}, \text{m}, \text{p}-\text{XCH}_2-\text{C}_6\text{H}_4-(\text{CH}_2)_n-\text{O}-(\text{CH}_2)_m-\text{CH}=\text{CH}_2$ ,

35  $\text{o}, \text{m}, \text{p}-\text{CH}_3\text{C}(\text{H})(\text{X})-\text{C}_6\text{H}_4-(\text{CH}_2)_n-\text{O}-(\text{CH}_2)_m-\text{CH}=\text{CH}_2$ ,

$\circ, m, p\text{-CH}_3\text{CH}_2\text{C(H)(X)-C}_6\text{H}_4\text{-(CH}_2\text{)}_n\text{O-(CH}_2\text{)}_m\text{CH=CH}_2$ ,  
 (in the above formulas, X is chlorine, bromine or iodine, n is an integer of 1 to 20, and m is an integer of 0 to 20; m is preferably an integer of 1 to 20);

- 5     $\circ, m, p\text{-XCH}_2\text{-C}_6\text{H}_4\text{O-(CH}_2\text{)}_n\text{CH=CH}_2$ ,  
 $\circ, m, p\text{-CH}_3\text{C(H)(X)-C}_6\text{H}_4\text{O-(CH}_2\text{)}_n\text{CH=CH}_2$ ,  
 $\circ, m, p\text{-CH}_3\text{CH}_2\text{C(H)(X)-C}_6\text{H}_4\text{O-(CH}_2\text{)}_n\text{CH=CH}_2$ ,  
 (in the above formulas, X is chlorine, bromine or iodine and n is an integer of 0 to 20; n is preferably an integer of 1 to 10 20);  
 $\circ, m, p\text{-XCH}_2\text{-C}_6\text{H}_4\text{O-(CH}_2\text{)}_n\text{O-(CH}_2\text{)}_m\text{CH=CH}_2$ ,  
 $\circ, m, p\text{-CH}_3\text{C(H)(X)-C}_6\text{H}_4\text{O-(CH}_2\text{)}_n\text{O-(CH}_2\text{)}_m\text{CH=CH}_2$ ,  
 $\circ, m, p\text{-CH}_3\text{CH}_2\text{C(H)(X)-C}_6\text{H}_4\text{O-(CH}_2\text{)}_n\text{O-(CH}_2\text{)}_m\text{CH=CH}_2$ ,  
 (in the above formulas, X is chlorine, bromine or iodine, n is 15 an integer of 1 to 20 and m is an integer of 0 to 20).

As the alkenyl-containing organic halide, there may further be mentioned compounds represented by the general formula 6:



- 20    (wherein R<sup>20</sup>, R<sup>21</sup>, R<sup>22</sup>, R<sup>24</sup> and X are defined above and R<sup>25</sup> is a direct bond, -C(O)O- (ester group), -C(O)- (keto group) or an o-, m- or p-phenylene group).

R<sup>24</sup> is a direct bond or a divalent organic group having 1 to 20 carbon atoms (which may contain one or more ether bonds) 25 and, when it is a direct bond, the vinyl group is bound to the carbon to which the halogen is bound, to form an allyl halide. In this case, the carbon-halogen bond is activated by the neighboring vinyl group, so that it is not always necessary for R<sup>25</sup> to be a C(O)O group or a phenylene group, for instance, but 30 it may be a direct bond. When R<sup>24</sup> is not a direct bond, R<sup>25</sup> is preferably a C(O)O group, C(O) group or phenylene group so that the carbon-halogen bond may be activated.

[0025]

As a specific example of compounds represented by the 35 general formula 6, there can be mentioned,

$\text{CH}_2=\text{CHCH}_2\text{X}$ ,  $\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_2\text{X}$ ,  
 $\text{CH}_2=\text{CHC(H)(X)CH}_3$ ,  $\text{CH}_2=\text{C}(\text{CH}_3)\text{C(H)(X)CH}_3$ ,  
 $\text{CH}_2=\text{CHC(X)(CH}_3)_2$ ,  $\text{CH}_2=\text{CHC(H)(X)C}_2\text{H}_5$ ,  
 $\text{CH}_2=\text{CHC(H)(X)CH(CH}_3)_2$ ,  
5     $\text{CH}_2=\text{CHC(H)(X)C}_6\text{H}_5$ ,  $\text{CH}_2=\text{CHC(H)(X)CH}_2\text{C}_6\text{H}_5$ ,  
 $\text{CH}_2=\text{CHCH}_2\text{C(H)(X)-CO}_2\text{R}$ ,  
 $\text{CH}_2=\text{CH}(\text{CH}_2)_2\text{C(H)(X)-CO}_2\text{R}$ ,  
 $\text{CH}_2=\text{CH}(\text{CH}_2)_3\text{C(H)(X)-CO}_2\text{R}$ ,  
 $\text{CH}_2=\text{CH}(\text{CH}_2)_8\text{C(H)(X)-CO}_2\text{R}$ ,  
10    $\text{CH}_2=\text{CHCH}_2\text{C(H)(X)-C}_6\text{H}_5$ ,  
 $\text{CH}_2=\text{CH}(\text{CH}_2)_2\text{C(H)(X)-C}_6\text{H}_5$ ,  
 $\text{CH}_2=\text{CH}(\text{CH}_2)_3\text{C(H)(X)-C}_6\text{H}_5$ ,  
(in the above formulas, X is chlorine, bromine or iodine, and  
R is an alkyl group having 1 to 20 carbon atoms, an aryl group  
15   having 6 to 20 carbon atoms, or an aralkyl group having 7 to  
20 carbon atoms). Among these, allyl chloride and allyl bromide  
are preferred from cost and availability viewpoint.  
[0026]

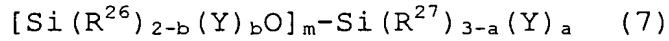
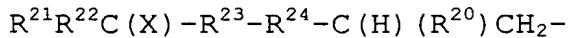
Specific examples of the alkenyl-containing sulfonyl  
20   halide are as follows:  
 $\text{o}-$ , m- or p- $\text{CH}_2=\text{CH-(CH}_2)_n\text{-C}_6\text{H}_4\text{-SO}_2\text{X}$  and  
 $\text{o}-$ , m- or p- $\text{CH}_2=\text{CH-(CH}_2)_n\text{-O-C}_6\text{H}_4\text{-SO}_2\text{X}$   
(wherein, in each formula, X is chlorine, bromine or iodine and  
n is an integer of 0 to 20; n is preferably an integer of 1 to  
25   20), among others.  
[0027]

When an alkenyl-containing initiator is used, care should  
be taken since there is a possibility that olefin of the  
initiator may also react with the polymerization terminus.  
30   Additionally, a polymer produced by using the  
alkenyl-containing initiator by itself becomes the polymer (I),  
but also has a growing terminus. The growing terminus may  
become not only a growing terminus of radical polymerization,  
but also an initiator of living cationic polymerization in which  
35   the polymer (I) is added. In this case, there may occur

undesirable polymerization reaction other than the bond of the polymers, which the present invention intends to. For avoiding this reaction, the growing terminus (in many cases, a halogen group) may be removed by an alkaline treatment, and the like.

5 [0028]

The crosslinking silyl-containing organic halide is not particularly restricted but includes, among others, those having a structure shown by the general formula 7:



(wherein  $R^{20}$ ,  $R^{21}$ ,  $R^{22}$ ,  $R^{23}$ ,  $R^{24}$  and  $X$  are as defined above,  $R^{26}$  and  $R^{27}$  each is an alkyl group having 1 to 20 carbon atoms, an aryl group having 6 to 20 carbon atoms, or an aralkyl group having 7 to 20 carbon atoms, or a triorganosiloxy group represented

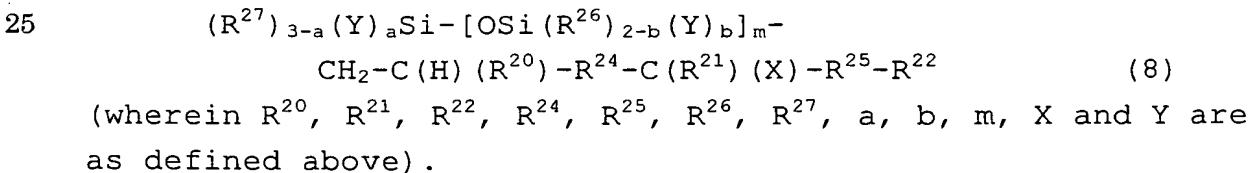
15 by  $(R')_3SiO^-$  (in which  $R'$  is a monovalent hydrocarbon group having 1 to 20 carbon atoms and the three  $R'$  groups may be the same or different) and, when there are two or more  $R^{26}$  and/or  $R^{27}$  groups, they may be the same or different,  $Y$  represents a hydroxyl group or a hydrolyzable group and, when there are two 20 or more  $Y$  groups, they may be the same or different,  $a$  represents 0, 1, 2 or 3,  $b$  represents 0, 1 or 2 and  $m$  is an integer of 0 to 19, provided that the relation  $a + mb \geq 1$  should be satisfied.

As a specific example of compounds represented by the general formula 7, there can be mentioned,

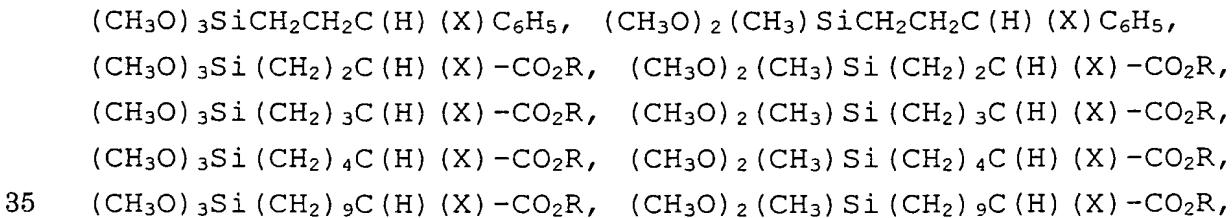
25  $XCH_2C(O)O(CH_2)_nSi(OCH_3)_3$ ,  $CH_3C(H)(X)C(O)O(CH_2)_nSi(OCH_3)_3$ ,  
 $(CH_3)_2C(X)C(O)O(CH_2)_nSi(OCH_3)_3$ ,  $XCH_2C(O)O(CH_2)_nSi(CH_3)(OCH_3)_2$ ,  
 $CH_3C(H)(X)C(O)O(CH_2)_nSi(CH_3)(OCH_3)_2$ ,  
 $(CH_3)_2C(X)C(O)O(CH_2)_nSi(CH_3)(OCH_3)_2$ ,  
30 (wherein, in each formula,  $X$  is chlorine, bromine or iodine and  $n$  is an integer of 0 to 20),  
 $XCH_2C(O)O(CH_2)_nO(CH_2)_mSi(OCH_3)_3$ ,  
 $H_3CC(H)(X)C(O)O(CH_2)_nO(CH_2)_mSi(OCH_3)_3$ ,  
 $(H_3C)_2C(X)C(O)O(CH_2)_nO(CH_2)_mSi(OCH_3)_3$ ,  
 $CH_3CH_2C(H)(X)C(O)O(CH_2)_nO(CH_2)_mSi(OCH_3)_3$ ,  
35  $XCH_2C(O)O(CH_2)_nO(CH_2)_mSi(CH_3)(OCH_3)_2$ ,

$\text{H}_3\text{CC}(\text{H})(\text{X})\text{C}(\text{O})\text{O}(\text{CH}_2)_n\text{O}(\text{CH}_2)_m\text{-Si}(\text{CH}_3)(\text{OCH}_3)_2$ ,  
 $(\text{H}_3\text{C})_2\text{C}(\text{X})\text{C}(\text{O})\text{O}(\text{CH}_2)_n\text{O}(\text{CH}_2)_m\text{-Si}(\text{CH}_3)(\text{OCH}_3)_2$ ,  
 $\text{CH}_3\text{CH}_2\text{C}(\text{H})(\text{X})\text{C}(\text{O})\text{O}(\text{CH}_2)_n\text{O}(\text{CH}_2)_m\text{-Si}(\text{CH}_3)(\text{OCH}_3)_2$ ,  
 (wherein, in each formula, X is chlorine, bromine or iodine,  
 5 n is an integer of 0 to 20, and m is an integer of 0 to 20),  
 $\text{o}, \text{m}, \text{p-XCH}_2\text{-C}_6\text{H}_4\text{-}(\text{CH}_2)_2\text{Si}(\text{OCH}_3)_3$ ,  
 $\text{o}, \text{m}, \text{p-CH}_3\text{C}(\text{H})(\text{X})\text{-C}_6\text{H}_4\text{-}(\text{CH}_2)_2\text{Si}(\text{OCH}_3)_3$ ,  
 $\text{o}, \text{m}, \text{p-CH}_3\text{CH}_2\text{C}(\text{H})(\text{X})\text{-C}_6\text{H}_4\text{-}(\text{CH}_2)_2\text{Si}(\text{OCH}_3)_3$ ,  
 $\text{o}, \text{m}, \text{p-XCH}_2\text{-C}_6\text{H}_4\text{-}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$ ,  
 10  $\text{o}, \text{m}, \text{p-CH}_3\text{C}(\text{H})(\text{X})\text{-C}_6\text{H}_4\text{-}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$ ,  
 $\text{o}, \text{m}, \text{p-CH}_3\text{CH}_2\text{C}(\text{H})(\text{X})\text{-C}_6\text{H}_4\text{-}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$ ,  
 $\text{o}, \text{m}, \text{p-XCH}_2\text{-C}_6\text{H}_4\text{-}(\text{CH}_2)_2\text{-O-}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$ ,  
 $\text{o}, \text{m}, \text{p-CH}_3\text{C}(\text{H})(\text{X})\text{-C}_6\text{H}_4\text{-}(\text{CH}_2)_2\text{-O-}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$ ,  
 $\text{o}, \text{m}, \text{p-CH}_3\text{CH}_2\text{C}(\text{H})(\text{X})\text{-C}_6\text{H}_4\text{-}(\text{CH}_2)_2\text{-O-}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$ ,  
 15  $\text{o}, \text{m}, \text{p-XCH}_2\text{-C}_6\text{H}_4\text{-O-}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$ ,  
 $\text{o}, \text{m}, \text{p-CH}_3\text{C}(\text{H})(\text{X})\text{-C}_6\text{H}_4\text{-O-}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$ ,  
 $\text{o}, \text{m}, \text{p-CH}_3\text{CH}_2\text{C}(\text{H})(\text{X})\text{-C}_6\text{H}_4\text{-O-}(\text{CH}_2)_3\text{-Si}(\text{OCH}_3)_3$ ,  
 $\text{o}, \text{m}, \text{p-XCH}_2\text{-C}_6\text{H}_4\text{-O-}(\text{CH}_2)_2\text{-O-}(\text{CH}_2)_3\text{-Si}(\text{OCH}_3)_3$ ,  
 $\text{o}, \text{m}, \text{p-CH}_3\text{C}(\text{H})(\text{X})\text{-C}_6\text{H}_4\text{-O-}(\text{CH}_2)_2\text{-O-}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$ ,  
 20  $\text{o}, \text{m}, \text{p-CH}_3\text{CH}_2\text{C}(\text{H})(\text{X})\text{-C}_6\text{H}_4\text{-O-}(\text{CH}_2)_2\text{-O-}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$ ,  
 (wherein, in each formula, X is chlorine, bromine or iodine).

As further examples of the crosslinking silyl-containing organic halide, there may be mentioned those having a structure represented by the general formula 8:



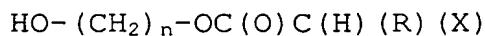
As a specific example of such compounds, there can be mentioned;



(CH<sub>3</sub>O)<sub>3</sub>Si(CH<sub>2</sub>)<sub>3</sub>C(H)(X)-C<sub>6</sub>H<sub>5</sub>, (CH<sub>3</sub>O)<sub>2</sub>(CH<sub>3</sub>)Si(CH<sub>2</sub>)<sub>3</sub>C(H)(X)-C<sub>6</sub>H<sub>5</sub>, (CH<sub>3</sub>O)<sub>3</sub>Si(CH<sub>2</sub>)<sub>4</sub>C(H)(X)-C<sub>6</sub>H<sub>5</sub>, (CH<sub>3</sub>O)<sub>2</sub>(CH<sub>3</sub>)Si(CH<sub>2</sub>)<sub>4</sub>C(H)(X)-C<sub>6</sub>H<sub>5</sub>, (wherein, in each formula, X is chlorine, bromine or iodine, R is an alkyl group having 1 to 20 carbon atoms, an aryl group having 6 to 20 carbon atoms, or an aralkyl group having 7 to 20 carbon atoms.), and the like.

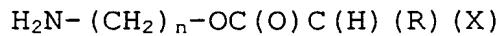
5 [0029]

The hydroxyl-containing organic halide or sulfonyl halide is not particularly restricted but includes compounds represented by the following formula:



(wherein X is chlorine, bromine or iodine, R is a hydrogen atom or an alkyl group having 1 to 20 carbon atoms, an aryl group having 6 to 20 carbon atoms, or an aralkyl group having 7 to 15 20 carbon atoms and n is an integer of 1 to 20).

The amino-containing organic halide or sulfonyl halide is not particularly restricted but includes compounds represented by the following formula:

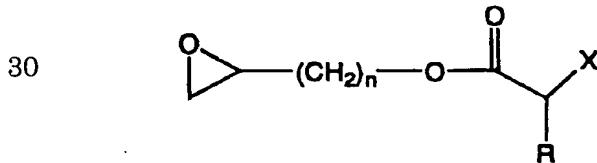


20 (wherein X is chlorine, bromine or iodine, R is a hydrogen atom or an alkyl group having 1 to 20 carbon atoms, an aryl having 6 to 20 carbon atoms, or an aralkyl group having 7 to 20 carbon atoms and n is an integer of 1 to 20).

The epoxy-containing organic halide or sulfonyl halide 25 is not particularly restricted but includes compounds represented by the following formula:

[0030]

[Chemical 5]



[0031]

(wherein X is chlorine, bromine or iodine, R is a hydrogen atom or an alkyl group having 1 to 20 carbon atoms, an aryl group

having 6 to 20 carbon atoms, or an aralkyl group having 7 to 20 carbon atoms and n is an integer of 1 to 20).

<Monomer>

The vinyl monomer to be used in controlled radical  
5 polymerization of the present invention is not particularly  
restricted and those mentioned above may be used.

[0032]

For introducing the group represented by the general  
formula 2 to the terminus, although it is not particularly  
10 restricted, preferably, the monomer represented by the general  
formula 4 is polymerized finally. When the monomer represented  
by the general formula 4 is polymerized from the beginning, it  
can be used as such, but when the other monomer is polymerized,  
it is necessary to add the monomer represented by the general  
15 formula 4 at the terminal stage of polymerization.

<Catalyst>

The transition metal complex to be used as a  
polymerization catalyst is not particularly restricted but  
preferably are complexes of monovalent copper, copper (valence:  
20 zero), divalent ruthenium, divalent iron or divalent nickel.  
Among them, copper complexes are preferred in view of cost and  
reaction controllability. Specific examples of monovalent  
copper compounds are cuprous chloride, cuprous bromide, cuprous  
iodide, cuprous cyanide, cuprous oxide, cuprous perchlorate and  
25 the like. When a copper compound is used, a ligand, such as  
2,2'-bipyridyl or a derivative thereof, 1,10-phenanthroline or  
a derivative thereof or a polyamine such as  
tetramethylethylenetriamine (TMEDA),  
pentamethyldiethylenetriamine or hexamethyl  
30 (2-aminoethyl)amine, is added to enhance the catalytic activity.  
A tristriphenylphosphine complex of divalent ruthenium  
chloride ( $\text{RuCl}_2(\text{PPh}_3)_3$ ) is also suited for use as a catalyst.  
When a ruthenium compound is used as a catalyst, an aluminum  
alkoxide is added as an activator. Furthermore, a  
35 bistriphenylphosphine complex of divalent iron ( $\text{FeCl}_2(\text{PPh}_3)_2$ ),

a bistriphenylphosphine complex of divalent nickel ( $\text{NiCl}_2(\text{PPh}_3)_2$ ) and a bistributylphosphine complex of divalent nickel ( $\text{NiBr}_2(\text{PBu}_3)_2$ ) are also suited as a catalysts.

<Solvent and temperature>

5       The above-mentioned atom transfer radical polymerization can be carried out in the absence or presence of various solvents. As the solvent, there may be mentioned, among others, hydrocarbon solvents such as benzene and toluene; ether solvents such as diethyl ether and tetrahydrofuran; halogenated 10 hydrocarbon solvents such as methylene chloride and chloroform; ketone solvents such as acetone, methyl ethyl ketone and methyl isobutyl ketone; alcohol solvents such as methanol, ethanol, propanol, isopropanol, n-butyl alcohol and tert-butyl alcohol; nitrile solvents such as acetonitrile, propionitrile and 15 benzonitrile; ester solvents such as ethyl acetate and butyl acetate; and carbonate solvents such as ethylene carbonate and propylene carbonate. These may be used singly or two or more of them may be used in admixture. The above polymerization can be conducted within the temperature range of room temperature 20 to 200°C, preferably 50°C to 150°C.

<Terminus conversion method>

When an initiator containing a functional group other than the general formula 1 is used, the polymer (I) is produced by being converted into the group represented by the general 25 formula 1 by some conversion reaction.

[0033]

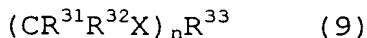
The converting method is not particularly restricted, but there may be mentioned the following methods.

As a functional group-containing initiator, those 30 mentioned above can be used, but a hydroxyl group is preferred. For converting the hydroxyl group, there may be mentioned various methods. It is not particularly restricted, but there may be mentioned, a method using a compound having the group represented by the general formula 1 and a group capable of 35 reacting with the hydroxyl group. As the group capable of

reacting with the hydroxyl group, there may be mentioned an isocyanate group and isothiocyanate group. As the compound having these group and the group represented by the general formula 1, there may be mentioned allyl isocyanate, allyl  
5 isothiocyanate, or the like.

**<Living cationic polymerization>**

In the practice of the present invention, the living cationic polymerization for producing the block copolymer by adding the above polymer (I) comprises polymerizing a  
10 cationically polymerizable monomer in the presence of a compound of the following general formula 9:



(wherein X is a substituent selected from a halogen atom, an alkoxy group having 1 to 6 carbon atoms and an acyloxy group,  
15 R<sup>31</sup> and R<sup>32</sup> may be the same or different and each is a hydrogen atom or a monovalent hydrocarbon group having 1 to 6 carbon atoms, R<sup>33</sup> is a polyvalent aromatic or aliphatic hydrocarbon group and n is a natural number of 1 to 6).

While the growing terminus of the living cationic  
20 polymerization is added to the group represented by the general formula 1 of the polymer (I), the group represented by the general formula 2 serves as an initiator of the living cationic polymerization. As the result, a multiblock copolymer is produced.

**25 <Monomer>**

The monomer to be used for the living cationic polymerization according to the present invention is not particularly restricted but includes, for example, aliphatic olefins, aromatic vinyls, dienes, vinyl ethers, silanes,  
30 vinylcarbazole, β-pinene, acenaphthylene and like monomers. These are used singly or two or more of them are used combinedly. Specific examples of the monomer are shown below. From the viewpoint of physical properties of the product copolymers, isobutylene is preferred among others.

35 [0034]

As the aliphatic olefin monomers, there may be mentioned isobutylene, ethylene, propylene, 1-butene, 2-methyl-1-butene, 3-methyl-1-butene, pentene, hexene, cyclohexene, 4-methyl-1-pentene, vinylcyclohexene, octene, norbornene and  
5 the like.

As the aromatic vinyl monomers, there may be mentioned styrene, o-, m- or p-methylstyrene,  $\alpha$ -methylstyrene,  $\beta$ -methylstyrene, 2,6-dimethylstyrene, 2,4-dimethylstyrene,  $\alpha$ -methyl-o-methylstyrene,  
10  $\alpha$ -methyl-m-methylstyrene,  $\alpha$ -methyl-p-methylstyrene,  $\beta$ -methyl-o-methylstyrene,  $\beta$ -methyl-m-methylstyrene,  $\beta$ -methyl-p-methylstyrene, 2,4,6-trimethylstyrene,  $\alpha$ -methyl-2,6-dimethylstyrene,  $\alpha$ -methyl-2,4-dimethylstyrene,  $\beta$ -methyl-2,6-dimethylstyrene,  $\beta$ -methyl-2,4-dimethylstyrene,  
15 o-, m- or p-chlorostyrene, 2,6-dichlorostyrene, 2,4-dichlorostyrene,  $\alpha$ -chloro-o-chlorostyrene,  $\alpha$ -chloro-m-chlorostyrene,  $\alpha$ -chloro-p-chlorostyrene,  $\beta$ -chloro-o-chlorostyrene,  $\beta$ -chloro-m-chlorostyrene,  $\beta$ -chloro-p-chlorostyrene, 2,4,6-trichlorostyrene,  
20  $\alpha$ -chloro-2,6-dichlorostyrene,  $\alpha$ -chloro-2,4-dichlorostyrene,  $\beta$ -chloro-2,6-dichlorostyrene,  $\beta$ -chloro-2,4-dichlorostyrene, o-, m- or p-t-butylstyrene, o-, m- or p-methoxystyrene, o-, m- or p-chloromethylystyrene,  
25 o-, m- or p-bromomethylystyrene, silyl-substituted styrene derivatives, indene, vinylnaphthalene and the like.

[0035]

As the diene monomers, there may be mentioned butadiene, isoprene, cyclopentadiene, cyclohexadiene, dicyclopentadiene, divinylbenzene, ethylenenorbornene and the like.  
30 As the vinyl ether monomers, there may be mentioned methyl vinyl ether, ethyl vinyl ether, (n-, iso)propyl vinyl ether, (n-, sec-, tert-, iso)butyl vinyl ether, methyl propenyl ether, ethyl propenyl ether and the like.

[0036]

35 As the silane compounds, there may be mentioned

vinyltrichlorosilane, vinylmethyldichlorosilane,  
 vinyldimethylchlorosilane, vinyldimethylmethoxysilane,  
 vinyltrimethylsilane, divinyldichlorosilane,  
 divinyldimethoxysilane, divinyldimethylsilane,

- 5 1,3-divinyl-1,1,3,3-tetramethyldisiloxane,  
 trivinylmethylsilane,  $\gamma$ -methacryloyloxy-  
 propyltrimethoxysilane,  $\gamma$ -methacryloyloxypropyl-  
 methyldimethoxysilane and the like.

<Initiator>

- 10 The above-mentioned compound of the general formula 9  
 serves as an initiator and forms a carbon cation in the presence  
 of a Lewis acid and the like, and carbon cation presumably serves  
 as a site of initiation of cationic polymerization. As examples  
 15 of the compound of the general formula 9 to be used in the present  
 invention, there may be mentioned the following:

[0037]

(1-chloro-1-methylethyl)benzene [ $C_6H_5C(CH_3)_2Cl$ ],  
 1,4-bis(1-chloro-1-methylethyl)benzene  
 [1,4-Cl( $CH_3$ )<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>C( $CH_3$ )<sub>2</sub>Cl],  
 20 1,3-bis(1-chloro-1-methylethyl)benzene  
 [1,3-Cl( $CH_3$ )<sub>2</sub>CC<sub>6</sub>H<sub>4</sub>C( $CH_3$ )<sub>2</sub>Cl],  
 1,3,5-tris(1-chloro-1-methylethyl)benzene  
 [1,3,5-(ClC( $CH_3$ )<sub>2</sub>)<sub>3</sub>C<sub>6</sub>H<sub>3</sub>],  
 1,3-bis(1-chloro-1-methylethyl)-(5-tert)-butylbenzene  
 25 [1,3-(C( $CH_3$ )<sub>2</sub>Cl)<sub>2</sub>-5-(C( $CH_3$ )<sub>3</sub>)C<sub>6</sub>H<sub>3</sub>]

[0038]

- Particularly preferred among them are  
 bis(1-chloro-1-methylethyl)benzenes [ $C_6H_4(C(CH_3)_2Cl)_2$ ]  
 (bis(1-chloro-1-methylethyl)benzenes are also called bis( $\alpha$ -  
 30 -chloroisopropyl)benzenes, bis(2-chloro-2-propyl)benzenes or  
 dicumyl chlorides). These are bifunctional initiators and,  
 when the polymerization is started with these, polymers having  
 growing termini at both ends are obtained and these, upon  
 reaction with the polymer (I), readily give multiblock  
 35 copolymers.

[0039]

Furthermore, in the present invention, it is allowable to use the polymer (I) as an initiator without using or using in combination with the above-mentioned initiator. In this case, living cationic polymerization is started from the group represented by the general formula 2 in the polymer (I), and a multiblock copolymer is produced by adding a growing terminus of the living cationic polymerization to the group represented by the general formula 1 in the polymer (I). When the polymer (I) alone is used as an initiator, the number of a growing terminus and an alkenyl group to be added are equal in principle, therefore a multiblock copolymer which is unlimitedly extended is obtained.

## &lt;Catalyst&gt;

The living cationic polymerization may be carried out in the presence of a Lewis acid catalyst. Such Lewis acid may be any of those which can be used in cationic polymerization. Suited for use are, for example, metal halides such as  $TiCl_4$ ,  $TiBr_4$ ,  $BCl_3$ ,  $BF_3$ ,  $BF_3 \cdot OEt_2$ ,  $SnCl_4$ ,  $SbCl_5$ ,  $SbF_5$ ,  $WCl_6$ ,  $TaCl_5$ ,  $VCl_5$ ,  $FeCl_3$ ,  $ZnBr_2$ ,  $AlCl_3$  and  $AlBr_3$ ; and organometal halides such as  $Et_2AlCl$  and  $EtAlCl_2$ . Considering the catalytic acitivity and commercial availability,  $TiCl_4$ ,  $BCl_3$  and  $SnCl_4$  are preferred. The amount of the Lewis acid to be used is not particularly restricted but can be selected according to the polymerization characteristics or concentration of the monomer employed. Generally, the catalyst is used in an amount of 0.1 to 100 mole equivalents, preferably 1 to 60 mole equivalents, relative to the compound of the general formula 12.

## &lt;Electron-donating component &gt;

The living cationic polymerization may also be carried out, when necessary, in the presence of an electron-donating component. Said electron-donating component is considered to have a stabilizing effect on growing carbon cations in cationic polymerization and, upon adding such electron donor, polymers having a controlled structure narrow in molecular weight

distribution are formed. The electron-donating component which can be used is not particularly restricted but includes, among others, pyridines, amines, amides, sulfoxides, esters and metal compounds having an oxygen atom bound to the metal atom.

5 [0040]

The amount of use of each component can adequately be designed according to the characteristics of the desired polymer. First, the molecular weight of the product polymer can be determined based on the mole equivalent relationship 10 between the cationically polymerizable monomer other than the isobutylenic monomer and isobutylene and the compound of the general formula 9. Generally, designing is made so that the product block copolymer may have a number average molecular weight of about 20,000 to 500,000.

15 <Polymerization conditions>

The present invention can be carried out in a solvent, if necessary. Any solvent can be used without any particular limitation provided that it will not substantially inhibit the cationic polymerization. Typically, there may be mentioned 20 halogenated hydrocarbons such as methyl chloride, dichloromethane, chloroform, ethyl chloride, dichloroethane, n-propyl chloride, n-butyl chloride and chlorobenzene; benzene and alkylbenzenes such as toluene, xylene, ethylbenzene, propylbenzene and butylbenzene; straight-chain aliphatic 25 hydrocarbons such as ethane, propane, butane, pentane, hexane, heptane, octane, nonane and decane; branched aliphatic hydrocarbons such as 2-methylpropane, 2-methylbutane, 2,3,3-trimethylpentane and 2,2,5-trimethylhexane; alicyclic hydrocarbons such cyclohexane, methylcyclohexane and 30 ethylcyclohexane; paraffin oils purified from petroleum fractions by hydrogenation; and the like. Among these, toluene-containing mixed solvents are preferred in view of safety to the environment and polymerization physical properties. Primary and/or secondary monohalogenated 35 hydrocarbons containing 3 to 8 carbon atoms are also preferably

used. As specific examples of such that can be used are 1-chloropropane, 1-chloro-2-methylpropane, 1-chlorobutane, 1-chloro-2-methylbutane, 1-chloro-3-methylbutane, 1-chloro-2,2-dimethylbutane, 1-chloro-3,3-dimethylbutane, 5 1-chloro-2,3-dimethylbutane, 1-chloropentane, 1-chloropentane, 1-chloro-2-methylpentane, 1-chloro-3-methylpentane, 1-chloro-4-methylpentane, 1-chlorohexane, 1-chloro-2-methylhexane, 1-chloro-3-methylhexane, 1-chloro-4-methylhexane, 10 1-chloro-5-methylhexane, 1-chloroheptane, 1-chlorooctane, 2-chloropropane, 2-chlorobutane, 2-chloropentane, 2-chloropentane, 2-chlorohexane, 2-chloroheptane, 2-chlorooctane and chlorobenzene. These may be used singly or two or more of them may be used in combination. Among them, 15 1-chlorobutane is preferred from the viewpoint of equilibrium among solubility of isobutylene-derived block copolymers, ease of decomposition for rendering the same nonhazardous, cost and other factors.

[0041]

20 These solvents are used singly or in combination considering the balance between the polymerization characteristics of the monomers constituting the block copolymer and the solubility of the product polymer, for instance.

25 The amount of solvent to be used is selected, considering the viscosity of the polymer solution to be obtained and the ease of removal of heat, so that the polymer concentration may be 1 to 50% by weight, preferably 5 to 35% by weight.

[0042]

30 In practicing the polymerization, the respective components are mixed up with cooling, for example at a temperature of -100°C to not higher than 0°C. A particularly preferred temperature range for attaining a balance between the cost of energy and the stability of polymerization is -30°C to 35 -80°C.

## &lt;Addition of polymer (I)&gt;

The time for adding the polymer (I) to the living cationic polymerization system is not particularly restricted but should be adequate to the production of the desired multiblock copolymer. There may be mentioned, for example, the technique already mentioned hereinabove which comprises adding it as an initiator from the initial stage of polymerization, the technique which comprises adding it during polymerization, and the technique which comprises adding it at the point of time of completion of the polymerization and adding simultaneously or later the cationically polymerizable monomer again. The point of time of completion of the polymerization is preferably the time point at which not less than 90%, more preferably not less than 99% of the monomer has been polymerized. Mere addition of the polymer (I) thereafter hardly results in multiblock formation and one more addition of the cationically polymerizable monomer is required. If this time of addition is too late, the terminus of the general formula 2 of the polymer (I) may possibly add directly to the terminus of the general formula 1; therefore, care should be taken.

[0043]

The amount of the polymer (I) is not particularly restricted but is preferably such that the number of growing termini in living cationic polymerization be equal to the number of termini represented by the general formula 1 in the polymer (I) to which said growing termini are to add. When the polymer (I) is used as an initiator from the beginning, the numbers are in principle equal to that of growing termini, as mentioned hereinabove. When another initiator is used, however, the number of growing termini becomes greater by the number of molecules of said initiator. It is therefore desirable to adjust the proportion thereof according to the desired multiblock copolymer.

[0044]

The polymer (I) may be added as such or in the form of

a solution in a solvent which will not adversely affect the living cationic polymerization.

<Uses>

<Thermoplastic elastomer>

5       The multiblock copolymer obtained by the production method of the present invention can be used in substantially the same fields of application as the existing styrenic elastomers. More specifically, it can be used for modifying resins or asphalt, for preparing compounds of the block  
10      copolymer with resins (with a plasticizer, a filler, a stabilizer, etc. added as occasion demands), as an antishrink agent for thermosetting resins, or as a base polymer for adhesives or pressure-sensitive adhesives or for damping materials. As specific fields of application, there may be  
15      mentioned automotive upholstery and exterior, electric and electronic fields, food wrapping films and tubes, drug containers or containers for medical use, sealable articles and the like.

<Impact resistance improving agent>

20      While the multiblock copolymer obtained by the production method of the present invention by itself can serve as a molding material as a resin having impact resistance, it can serve as an impact resistance improving agent as well for providing various thermoplastic resins and thermosetting resins with a  
25      high level of impact resistance when admixed with said resins. Further, it can also be used as a processability improving agent, compatibilizing agent, flattening agent, heat resistance modifier or the like. Furthermore, improvement of gas barrier property based on an isobutylene polymer can be expected.

30      [0045]

The thermoplastic resins which can be improved in shock resistance by addition of the multiblock copolymer of the present invention include, but are not limited to, polymethyl methacrylate resins, polyvinyl chloride resins, polyethylene resins, polypropylene resins, cyclic olefin copolymer resins,

polycarbonate resins, polyester resins, polycarbonate resin-polyester resin blends, homopolymers and copolymers obtained by polymerizing 70 to 100% by weight of at least one vinyl monomer selected from the group consisting of aromatic 5 alkenyl compounds, vinyl cyanide compounds and (meth)acrylic acid esters and 0 to 30% by weight of another vinyl monomer copolymerizable therewith, such as ethylene, propylene or vinyl acetate and/or a copolymerizable conjugated diene monomer, such as butadiene or isoprene, polystyrene resins, polyphenylene 10 ether resins, polystyrene-polyphenylene ether resin blends and the like. Said multiblock copolymer can be used in a wide variety of thermoplastic resins. In particular, polymethyl methacrylate resins, polyvinyl chloride resins, polypropylene resins, cyclic polyolefin resins, polycarbonate resins and 15 polyester resins, among others, are preferred since they can readily show its characteristics such as improved weathering resistance and impact resistance.

[0046]

As the method of adding the multiblock copolymer of the 20 present invention to various resins, there may be mentioned the method comprising mechanically mixing and shaping into pellets using a conventional apparatus such as a Banbury mixer, roll mill or twin-screw extruder. The pellets shaped by extrusion can be molded in a wide temperature range and, for molding, an 25 ordinary injection molding machine, blow molding machine or extrusion molding machine, for instance, is used.

[0047]

Furthermore, in the resulting resin compositions, there 30 may be incorporated one or more additives as necessary, including impact resistance improving agents, stabilizers, plasticizers, lubricants, flame retardants, pigments, fillers and the like. More specifically, there may be mentioned impact resistance improving agents such as methyl methacrylate-butadiene-styrene copolymers (MBS resins), 35 acrylic graft copolymers and acrylic-silicone composite rubber

type graft copolymers; stabilizers such as triphenyl phosphite; lubricants such as polyethylene wax and polypropylene wax; fire retardants such as phosphate fire retardants, e.g. triphenyl phosphate, tricresyl phosphate, bromine-containing fire retardants, e.g. decarbromobiphenyl, decabromodiphenyl ether, and antimony trioxide; pigments such as titanium oxide, zinc sulfide and zinc oxide; and filler such as glass fiber, asbestos, wollastonite, mica, talc and calcium carbonate.

[0048]

10 [Effect of the Invention]

By adding, according to the present invention, polymers containing an alkenyl group at one terminus and containing a group to be an initiator for living cationic polymerization at other terminus to a polymerization system for living radical polymerization, it is possible to obtain, with ease, multiblock copolymers resulting from binding of these polymers to one another. Furthermore, by producing the polymer to be added by controlled radical polymerization, further by living radical polymerization, multiblock copolymers well controlled in the molecular weight of the polymer block to be bound can be obtained.

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[Document Name] Abstract

[Abstract]

[Subject] The present invention has for its subject to provide a method of easily producing a multiblock copolymer composed of any of various polymers and a cationic polymerization polymer without requiring optimization of polymerization conditions which is difficult to achieve.

[Means for Solving] In the present invention, a block copolymer can be produced easily by adding a polymer (I) containing an alkenyl group at one terminus and containing a group to be an initiator for living cationic polymerization at other terminus to a living cationic polymerization system. Furthermore, said polymer (I) is produced by using controlled radical polymerization while easily being well controlled in the molecular weight. As the result, a block copolymer well controlled in the molecular weight of the polymer block to be bound can be obtained.

[Selective Figure] none